METHODS AND COMPOSITIONS FOR ENHANCING CONSOLIDATION STRENGTH OF PROPPANT IN SUBTERRANEAN FRACTURES

1. FIELD OF THE INVENTION.

[0001] The present invention relates to methods of forming one or more fractures in a subterranean zone with little or no closure pressure and consolidating proppant particles therein.

2. BACKGROUND OF THE INVENTION.

[0002] Hydrocarbon producing wells are often stimulated by hydraulic fracturing treatments. In hydraulic fracturing, a viscous gelled fracturing fluid which also functions as a carrier fluid is pumped into a subterranean zone to be fractured at a rate and pressure such that one or more fractures are formed in the zone. Proppant particles, e.g., graded sand, for propping the fractures open are suspended in the fracturing fluid. After forming the fracture(s), a viscosity breaker is used to cause the fracturing fluid to revert to a thin fluid, i.e., "break" the viscosity, after which the fracturing fluid can be returned to the surface. Once the viscosity of the fracturing fluid is broken, the proppant particles are deposited in the fractures and function to prevent the fractures from closing so that conductive channels are formed through which fluids can readily flow.

[0003] In order to prevent the subsequent flow-back of the proppant particles as well as loose or incompetent fines with fluids produced from the subterranean zone, the proppant particles have heretofore been coated with a hardenable resin composition which is caused to harden and consolidate the proppant particles in the zone. As a general rule, consolidation requires that closure stress must be applied to the proppant grains to insure resin coated particle-

to-particle contact. However, many hydraulic fractures do not completely close during the first 24 hours after fracturing treatments, especially in low-permeability formations. This results in poor consolidation. Poor consolidation allows proppant particles and formation fines to flow-back with produced formation fluids. The flow-back of the proppant particles and formation fines is very detrimental in that it erodes metal goods, plugs piping and vessels and causes damage to valves, instruments and other production equipment.

[0004] The resin coating of a pre-coated resin particle is already partially cured (hardened) to provide for storage and handling, so only a portion of the resin is available for hardening in the subterranean zone and thereby contributing to the ultimate consolidation strength. As the resin coated proppant is deposited in the fracture(s) and exposed to higher formation temperatures, the resin curing process is re-initiated. The more the resin coating cures or hardens before the resin coated proppant particles are brought into contact with each other, the lower the consolidation strength that will be developed.

[0005] Difficulty in achieving this contact is due in part to the gelled carrier fluid that forms a film of gelled carrier fluid on the surface of the resin coated proppant particles. This film significantly hinders contact between the resin coated proppant particles, and thus reduces the consolidation strength that can develop.

[0006] Thus, there are needs for improved methods of consolidating proppant particles in subterranean fractures whereby permeable packs of consolidated proppant particles are formed.

SUMMARY OF THE INVENTION

[0007] The present invention provides improved methods and compositions for consolidating proppant in fractures formed in subterranean zones which meet the needs described above and overcome the deficiencies of the prior art. The methods, pre-coated proppant

particles, and coating compositions of this invention include a gel breaker that facilitates removal of gelled carrier fluid from the surface of hardenable resin coated proppant particles and allows resin coated particle-to-particle contact, thus improving the consolidation strength.

[0008] An improved method of this invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein comprises the following steps. Proppant particles pre-coated with a hardenable resin coating composition are provided. The coating composition comprises a hardenable organic resin, a silane coupling agent and a gel breaker. A gelled liquid fracturing fluid is also prepared or provided and is pumped into the subterranean zone to form one or more fractures therein. The pre-coated proppant particles are mixed with the fracturing fluid being pumped whereby the pre-coated proppant particles are suspended therein. When the pre-coated proppant particles reach the fracture(s), the pumping of the fracturing fluid is terminated and the pre-coated proppant particles are deposited therein. Thereafter, the coating composition on the pre-coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more permeable packs.

[0009] Another improved method of this invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein comprises the following steps. Proppant particles pre-coated with a hardenable resin coating composition are provided. The coating composition comprises a hardenable organic resin selected from the group consisting of phenolic resin, furan resin, a mixture of phenolic and furan resin, a terpolymer of phenol, the reaction product of furfuryl alcohol with an aldehyde, resoles, a resole/novolak mixture, a bisphenol-aldehyde novolak polymer and a bisphenol homopolymer, a silane coupling agent, and a dimethyl glutarate gel breaker. A gelled liquid fracturing fluid is

also prepared or provided and is pumped into the subterranean zone to form one or more fractures. The pre-coated proppant particles are mixed with the fracturing fluid being pumped whereby the pre-coated proppant particles are suspended therein. When the pre-coated proppant particles reach the fracture(s), the pumping of the fracturing fluid is terminated and the pre-coated proppant particles are deposited therein. Thereafter, the coating composition on the pre-coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more permeable packs.

[0010] Pre-coated proppant particles of this invention comprise proppant particles and a coating composition comprising a hardenable organic resin, a silane coupling agent and a gel breaker. The improved coating composition of this invention for pre-coating proppant particles comprises a hardenable organic resin, a silane coupling agent and a gel breaker.

[0011] The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] The present invention provides improved methods and compositions for forming one or more fractures in a subterranean zone and consolidating proppant particles therein. A preferred method of the present invention of forming one or more fractures in a subterranean zone and consolidating proppant particles pre-coated with a hardenable coating therein comprises the following steps. Proppant particles pre-coated with a hardenable resin coating composition are provided. The coating composition comprises a hardenable organic resin, a silane coupling agent and a gel breaker. A gelled liquid fracturing fluid is also prepared or

provided and is pumped into the subterranean zone to form one or more fractures therein. The pre-coated proppant particles are mixed with the fracturing fluid being pumped whereby the pre-coated proppant particles are suspended therein. When the pre-coated proppant particles reach the fracture(s), the pumping of the fracturing fluid is terminated and the pre-coated proppant particles are deposited therein. Thereafter, the coating composition on the pre-coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more permeable packs.

[0013] The proppant particles utilized in accordance with the present invention are generally of a size such that formation particulate solids that migrate with produced fluids are prevented from being produced from the subterranean zone. Various kinds of proppant particles can be utilized including graded sand, bauxite, ceramic materials, glass materials, walnut hulls, polymer beads and the like. Generally, the proppant particles have a size in the range of from about 2 to about 400 mesh, U.S. Sieve Series. The preferred proppant is graded sand having a particle size in the range of from about 10 to about 70 mesh, U.S. Sieve Series. Preferred sand particle size distribution ranges are one or more of 10-20 mesh, 20-40 mesh, 40-60 mesh or 50-70 mesh, depending on the particular size and distribution of formation solids to be screened out by the consolidated proppant particles.

[0014] Hardenable resins suitable for use in the present invention include, but are not limited to, phenolic resin, furan resin, a mixture of phenolic and furan resin, a terpolymer of phenol, the reaction product of furfuryl alcohol with an aldehyde, resoles, resole/novolak mixtures, a bisphenol-aldehyde novolak polymer, and a bisphenol homopolymer. Preferrably the hardenable resin is a phenolic or furan resin and more preferably the hardenable resin is a

mixture of phenolic and furan resin. A suitable phenolic and furan resin mixture is available commercially from the Durez Corporation of Grand Island, NY.

[0015] The hardenable resin is the main constituent of the hardenable resin composition and is generally present in an amount in the range of from about 40% to about 70% by weight of the coating composition, and more preferably in an amount of from about 50% to about 60%.

[0016] Silane coupling agents are used to ensure good bonding between the hardenable organic resin and the proppant particle. Examples of silane coupling agents which can be utilized in the hardenable resin composition include, but are not limited to, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane. Of these, n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane is preferred. The silane coupling agent is included in the coating composition in an amount in the range of from about 0.1% to about 3% by weight of the composition and more preferably in an amount of from about 0.5% to about 2%.

[0017] Gel breakers are included in the coating composition to facilitate removal of the film of gelled carrier fluid that forms on the surface of the resin coated proppant particles. The gel breaker, and inclusion of the gel breaker in the coating composition, reduces the viscosity of the gel film separating adjacent resin coated proppant particles and allows the resin coated proppant particles to contact each other before the resin coating completely cures. The gel breaker component utilized in the encapsulated gel breaker can be, but is not limited to, oxidative breakers, delayed release acids, delayed release enzymes, temperature activated breakers, and hydrolyzable esters.

[0018] Examples of oxidative breakers suitable for use in the coating composition of this invention include, but are not limited to, organic peroxides, alkali metal persulfates, and alkali metal chlorites, bromates, chlorates, hypochlorites and permanganates.

[0019] Examples of delayed release acid breakers suitable for use in the coating composition of this invention include, but are not limited to, acetic anhydride and organic and inorganic acids such as fumaric acid, benzoic acid, sulfonic acid, phosphoric acids, aliphatic polyesters, poly lactic acid, poly(lactides), polyanhydrides, and poly(amino acids).

[0020] Delayed release enzyme breakers may be used to catalyze the hydrolysis of glycosidic bonds between the monomer units of polysaccharides in the gel, thus reducing the gel viscosity. Examples of suitable delayed release enzyme breakers suitable for use in the coating composition include, but are not limited to, alpha and beta amylases, exo- and endo-glucosidases, amyloglucosidase, oligoglucosidase, invertase, maltase, cellulase, hemicellulase, endo-xylanase and exo-xylanase. More preferred enzyme breakers are enzymes or combinations of enzymes that attack the glucosidic linkages of the cellulose polymer backbone and degrade the polymer into mostly monosaccharide and disaccharide units. Examples of such enzyme breakers include, but are not limited to, cellulase, hemicellulase, endo-glucosidase, exo-glucosidase, exo-xylanase and the like. The two most preferred enzyme breakers are exo- and endo-glucosidases.

[0021] Temperature activated breakers activate when the pre-coated proppant particles are heated by the subterranean zone in which they are placed, to the activation temperature of the breaker. Examples of suitable temperature activated breakers for use in the coating composition include, but are not limited to, alkaline earth metal peroxides such as calcium peroxide and magnesium peroxide, zinc peroxide and mixtures thereof.

[0022] Preferably, the present invention utilizes gel breakers that can complex with the gel crosslinking agent in the polymer gel. Examples of such gel breakers include, but are not limited to, hydrolyzable esters such as sorbitol, catechol, dimethyl glutarate and mixtures of dimethyl glutarate, dimethyl succinate and dimethyl adipate. More preferably the gel breaker is dimethyl glutarate.

[0023] The gel breaker utilized in the present invention is optionally encapsulated with a water soluble material or other encapsulating material using procedures known to those skilled in the art. The encapsulating material slowly releases the gel breaker. Examples of encapsulating materials that can be used include, but are not limited to, polyvinyl alcohol, polylactic acid, EPDM rubber, polyvinylidene chloride, nylon, waxes, polyurethanes, cross-linked partially hydrolyzed acrylics and surfactants.

[0024] Preferably, the gel breaker is present in the coating composition in an amount in the range of from about 0.1% to about 10% by weight thereof, and more preferably from about 1% to about 4%. The gel breaker may be added to the coating composition prior to coating the proppant particles, resulting in fairly uniform distribution of gel breaker in the coating composition. The gel breaker may also be added to the mixer just after the proppant particles have been coated and while the resin is still partially curing. In this case the gel breaker is distributed closer to the outer surface of the coating. Alternatively, the gel breaker may be coated onto proppant particles pre-coated with resin that has already partially cured. The gel breaker may be also coated onto resin pre-coated proppant on the fly at the well site as the pre-coated proppant is being pumped down hole during the hydraulic fracturing treatment. These last two methods result in the gel breaker being present mostly as an outer layer of the coating composition.

[0025] A number of other components may be added to the coating composition. For example, a catalyst can be added to the resin to reduce the time and temperature needed to partially cure the resin in the coating and produce individual, free flowing resin pre-coated proppant particles. Suitable catalysts generally include water soluble multivalent metal ion salts such as nitrates and chlorides, acids with a pKa of about 4.0 or lower, ammonia, and amine salts of acids with a pKa of about 4.0 or lower. Examples of suitable acids with a pKa of about 4.0 or lower include, but are not limited to, phosphoric, sulfuric, nitric, benzenesulfonic, toluenesulfonic, xylenesulfonic, sulfamic, oxalic and salicylic acids. Examples of suitable amine salts of acids with a pKa of about 4.0 or lower include, but are not limited to, amine nitrates such as ammonium nitrate, amine chlorides, amine sulfates and amine fluorides.

[0026] The coating composition is preferably pre-coated on the proppant particles in an amount ranging from about 0.1% to about 5% by weight of the proppant particles and more preferably from about 2% to about 4%.

[0027] A gelled liquid fracturing fluid is prepared or provided. The gelled liquid fracturing fluid is comprised of water and a gelling agent. Suitable gelling agents include, but are not limited to, guar gum, guar gum derivatives and cellulose derivatives. The gelling agent in the fracturing fluid is generally present in an amount in the range of from about 0.01% to about 4% by weight of water therein and more preferably in an amount of about 0.1% to about 2%. The gelled liquid fracturing fluid can include a cross-linking agent for increasing the viscosity of the fracturing fluid. Examples of suitable cross-linking agents include, but are not limited to, alkali metal borates, borax, boric acid and compounds capable of releasing multivalent metal ions in aqueous solutions. When used, the cross-linking agent is included in

the fracturing fluid in an amount in the range of from about 0.01% to about 3% by weight of water therein and more preferably in an amount of about 0.1% to about 2%.

[0028] The fracturing fluid generally also includes a delayed viscosity breaker which functions to reduce the viscosity of the fracturing fluid and cause the resin composition coated proppant particles suspended in the fracturing fluid to be deposited in the fractures. Delayed viscosity breakers which can be utilized include, but are not limited to, oxidizers and enzymes. When used, the delayed viscosity breaker is included in the fracturing fluid in an amount in the range of from about 0.01% to about 5% by weight of water therein.

[0029] A particularly suitable embodiment of this invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating pre-coated proppant particles therein comprises the following steps. Proppant particles pre-coated with a hardenable resin coating composition are prepared or provided. The coating composition comprises a hardenable organic resin selected from the group consisting of a mixture of phenolic and furan resin, a terpolymer of phenol, furfuryl alcohol and an aldehyde, resoles, resole/novolak mixtures, a bisphenol-aldehyde novolak polymer, and a bisphenol homopolymer, a silane coupling agent and an gel breaker comprising a mixture of hydrolyzable esters. A gelled liquid fracturing fluid is also prepared or provided and is pumped into the subterranean zone to form one or more fractures therein. The pre-coated proppant particles are mixed with the fracturing fluid being pumped whereby the pre-coated proppant particles are suspended therein. When the pre-coated proppant particles reach the fracture(s), the pumping of the fracturing fluid is terminated and the pre-coated proppant particles are deposited therein. Thereafter, the coating composition on the pre-coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0030] Preferred pre-coated proppant particles of this invention comprise proppant particles coated with a coating composition comprising a hardenable organic resin, a silane coupling agent and a gel breaker. The pre-coated proppant particles are described above in the discussion of methods of this invention.

[0031] Preferred coating compositions of this invention comprise a hardenable organic resin, a silane coupling agent and a gel breaker. Preferred compositions are described above in the discussion of methods of this invention.

[0032] A preferred method of forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein comprises the steps of: (a) providing proppant particles pre-coated with a coating composition comprising a hardenable organic resin, a silane coupling agent and a gel breaker; (b) preparing or providing a gelled liquid fracturing fluid; (c) pumping the gelled liquid fracturing fluid into the subterranean zone to form one or more fractures; (d) mixing the proppant particles pre-coated with the coating composition with the fracturing fluid pumped in accordance with step (c) whereby the pre-coated proppant particles are suspended therein; (e) when the pre-coated proppant particles reach the one or more fractures, terminating the pumping of the fracturing fluid; and (f) allowing the coating composition on the pre-coated proppant particles to harden by heat and consolidate the proppant particles into one or more permeable packs.

[0033] Thus, the present invention is well adapted to attain the objects and advantages mentioned as well as those that are inherent within. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

[0034] What is claimed is: